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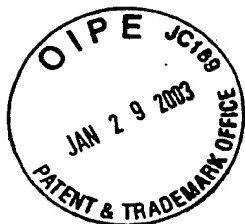
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I, Keiji Tokieda, of 2-20-204, Kaitori 2-chome, Tama-shi, Tokyo,
Japan, a translator, being duly sworn, depose and say:

1. That I am well acquainted with the Japanese and English languages; and
2. That the attached translation is a true translation into English of the
Certified copy of the Japanese Patent Application No. 275976/96 filed on
October 18, 1996.

Dated: May 29, 2002

Keiji Tokieda



PATENT OFFICE
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This is to certify that the annexed is a true copy
of the following application as filed with this Office.

Date of Application: October 18, 1996

Application Number: 275976/96

Applicant(s): Akira Kishimoto

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January 9, 1998

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Title of Invention: Oxygen-absorbing resin composition,
packing container, and process for the same

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(Name of the Document) SPECIFICATION

(Title of the Invention)

OXYGEN-ABSORBING RESIN COMPOSITION,

PACKING CONTAINER, AND PROCESS FOR THE SAME

(Scope of Claims)

1. An oxygen-absorbing resin composition obtained by blending 10 to 200 parts by weight of an oxygen-absorbing agent particles per 100 parts by weight of the thermoplastic resin, which comprise a reducing iron powder and an oxidation-promoting agent or a catalyst layer firmly adhered and coated to surfaces of said reducing iron powder, and which has a specific surface area of not smaller than $0.5 \text{ m}^2/\text{g}$ and an apparent density of not larger than 2.2 g/cc , and in which the oxidation-promoting agent or the catalyst is present in an amount of from 0.1 to 5 % by weight per the reducing iron powder.

2. An oxygen-absorbing resin composition according to claim 1, wherein the oxygen-absorbing agent particles have a flat shape or a spindle shape and wherein the particles having an average particle diameter of from 10 to $50 \text{ }\mu\text{m}$ as measured by the laser-scattering method and an aspect ratio (short axis size/long axis size) of not larger than 0.6 are present in an amount of not smaller than 50%, and the compression degree of the particles is not smaller than 20%.

3. An oxygen-absorbing resin composition according to claim 1, wherein the oxygen-absorbing agent particles are obtained by dry-milling a reducing iron powder and a powder of an oxidation-promoting agent or a catalyst.

4. An oxygen-absorbing resin composition according to claim 1, wherein the thermoplastic resin is a blend of a plurality of substantially incompatible thermoplastic resins or elastomers.

5. A packaging container according to any one of claims 1 to 4, which includes a layer of oxygen-absorbing resin composition as a container wall.

6. A packaging container for heat sterilization according to any one of claims 1 to 4, which includes a layer of oxygen-absorbing resin composition as a container wall.

7. A process for preparing a sterilized and sealed packaging body, wherein a content having a water content of not less than 50 % by weight is filled in a packaging container having a layer of oxygen-absorbing resin composition according to any one of claims 1 to 4 as a container wall, sealed and heat-sterilized.

(Detailed Description of the Invention)

(Technical Field to which the Invention Belongs)

The present invention relates to an oxygen-absorbing resin composition and a packaging container using the same.

More specifically, the invention relates to an oxygen-absorbing resin composition and a packaging container having a large oxygen-absorbing rate, without causing any change in appearance after preserved for extended periods of time after the retort sterilization, and exhibiting excellent appearance.

(Prior Art)

Metal cans, glass bottles and various plastic containers have heretofore been used as packaging containers. Among them, plastic containers have been used in a variety of applications owing to their light weights, shock resistance and cost.

However, though no oxygen is permitted to permeate through the walls of the metal cans and glass bottles, oxygen permeates through the walls of the plastic containers to an extent that cannot be neglected, arousing a problem from the standpoint of preserving the contents.

Conventionally, in order to capture the oxygen remaining in the container, or to capture the oxygen permeating through the container wall, it has been known to incorporate an oxygen-absorbing agent or an deoxidizer in the resin. For example, in Japanese Unexamined Patent Publication No. 194959/1982, there is described a container lid comprising a container lid hull and a gasket for sealing provided in the sealed portion of the hull, wherein

a solid oxygen-absorbing agent is contained in the gasket for sealing.

Furthermore, in Japanese Unexamined Patent Publication No. 278244/1989, there is described a multi-layer plastic container characterized in that it has a resin composition layer in which a deoxidizer and dehydrator are incorporated in a gas-barrier resin having an oxygen permeation coefficient of not higher than 10^{-12} cc•cm/cm²•sec•cmHg at 20°C and 0 % RH, and having a water absorption of not less than 0.5 % by weight at 20°C and 100 % RH.

Using the iron powder coated with an oxidation-promoting agent or the like on the surface thereof as the oxygen-absorbing agent has also been known. In Japanese Unexamined Patent Publication No. 14185/1978, there is described an oxygen-absorbing agent comprising a metal powder coated with a metal halide, in which the coated amount of the metal halide is 0.001 - 5 parts per 100 parts of the metal powder, and the water content is less than 1% by weight of the whole weight.

Incorporating an oxygen-absorbing agent comprising an iron powder coated with an oxidation-promoting agent in advance into the resin has also been known. In the above-mentioned Japanese Unexamined Patent Publication No. 194959/1982, it is described that iron powder or the like coated with metal halide can be used as the oxygen-

absorbing agent. Furthermore, in Japanese Unexamined Patent Publication No. 72851/1990, there is described a deoxidizer composition-containing fine porous film obtained by drawing a thermoplastic resin film obtained by dispersing a deoxidizer composition in the film, and it is also described to use an iron powder coated with metal salt halide on the surface thereof as the above-mentioned deoxidizer component. Furthermore, in Japanese Unexamined Patent Publication No. 170940/1994, there is described a production process of an oxygen-absorbing sheet, which comprises kneading a mixture of 30 to 85 parts by weight of iron powder having a primary particle size of from 0.01 to 20 μm and agglomerated particle size of from 5 to 200 μm and an electrolyte aqueous solution, with 15 ~ 70 parts by weight of a thermoplastic resin, making the kneaded product into a sheet, and drawing the sheet at least in one axial direction at the magnification of 1.5 ~ 9.

(Problems that the Invention is to Solve)

With the known resin composition blended with oxygen-absorbing agent, an oxidation-promoting agent such as metal salt halide or the like absorbs the water, and the oxygen-absorbing agent such as iron powder or the like is oxidized under the existence of this water, thereby the oxygen in the container or the oxygen passing through the container wall is absorbed.

The known resin composition blended with oxygen-absorbing agent, however, needs long time for absorbing the oxygen within the container, thus it does not have a sufficiently high oxygen-absorbing rate, or does not have a satisfactory content-preserving property.

Furthermore, even if the known resin composition blended with oxygen-absorbing agent has satisfactory appearance properties, such as smoothness and the like when the resin composition is molded into a container, ruggedness is caused on the surface, and in an undue case, a crack is recognized in the resin composition layer, while the container is kept for a long period of time, or subjected to the heat sterilization such as the retort sterilization.

The object of the present invention, therefore, is to provide a resin composition containing an oxygen-absorbing agent having improved oxygen-absorbing rate, and excellent appearance, without causing ruggedness after being kept for a long period of time or after being heat-sterilized, and a packaging container molded from said resin composition.

Another object of the present invention is to provide a production process of the sealed packaging body which can suppress the oxygen level in the container to a low level, and can maintain the appearance after the heat sterilization at an excellent level.

Means of Solving the Problems

According to the present invention, there is provided an oxygen-absorbing resin composition obtained by blending 10 to 200 parts by weight of an oxygen-absorbing agent particles per 100 parts by weight of the thermoplastic resin, which comprise a reducing iron powder and an oxidation-promoting agent or a catalyst layer firmly adhered and coated to surfaces of said reducing iron powder, and which has a specific surface area of not smaller than $0.5 \text{ m}^2/\text{g}$ and an apparent density of not larger than 2.2 g/cc , and in which the oxidation-promoting agent or the catalyst is present in an amount of from 0.1 to 5 % by weight per the reducing iron powder.

According to the present invention, there is provided a packaging container for heat sterilization which includes a layer of the above-mentioned oxygen-absorbing resin composition as a container wall.

Moreover, according to the present invention, there is provided a process for preparing a sterilized and sealed packaging body, wherein a content having a water content of not less than 50 % by weight is filled in a packaging container having a layer of the above-mentioned oxygen-absorbing resin composition as a container wall, sealed and heat-sterilized.

In the resin composition blended with the oxygen-

absorbing agent used in the present invention, it is desired that:

1. The particles having a flat shape or a spindle shape and wherein the particles having an average particle diameter of from 10 to 50 μm as measured by the laser-scattering method and an aspect ratio (short axis size/long axis size) of not larger than 0.6 are present in an amount of not smaller than 50%, and the compression degree of the particles is not smaller than 20%;

2. The oxygen-absorbing agent particles are obtained by dry-milling a reducing iron powder and a powder of an oxidation-promoting agent or a catalyst; and

3. The thermoplastic resin is a blend of a plurality of substantially incompatible thermoplastic resin or elastomers.

Working Examples of the Invention

In the present invention, the oxygen-absorbing agent particles to be mixed into the thermoplastic resin comprise a reducing iron powder and a layer of an oxidation-promoting agent or a catalyst firmly adhered and coated to surfaces of the reducing iron powder, and, particularly, contain the oxidation-promoting agent or the catalyst in an amount of from 0.1 to 5% by weight per the reducing iron powder and have a specific surface area of not smaller than 0.5 m^2/g and an apparent density of not larger than 2.2

g/cc.

In this specification, the layer of the oxidation-promoting agent or the catalyst firmly adhered and coated to surfaces of the reducing iron powder means not only that the oxidation-promoting agent or the catalyst is present or adhered to the surfaces of the reducing iron particles but also that the layer of the oxidation-promoting agent or the catalyst remains firmly adhered on the surfaces of the reducing iron powder without substantially being peeled off even under the condition of being kneaded together with the thermoplastic resin.

Referring to Fig. 1 schematically illustrating the structure of the oxygen-absorbing agent particles used in the present invention, a particle 10 comprises a core particle 20 of a reducing iron powder and a layer 30 of the oxidization-promoting agent or the catalyst firmly adhered to the surface thereof, the particle having a long axis size a and a short axis size b .

When the surfaces of the reducing iron powder are simply coated with the oxidation-promoting agent or the catalyst, the oxidation-promoting agent particles or the catalyst particles split off the surfaces of the reducing iron particles when being kneaded together with the thermoplastic resin, and the reducing iron free particles and the oxidation-promoting agent particles or the catalyst

free particles are made present in the resin composition. This also occurs even when the oxidation promoting agent is applied to the iron powder using an aqueous solution, since the oxidation-promoting agents precipitate in the form of crystals. The oxidation-promoting agent or the catalyst in the resin composition absorbs the water that has permeated into the resin. However, since a distance is maintained relative to the reducing iron particles, the reducing iron powder is not quickly oxidized and the oxygen-absorbing rate becomes small. Besides, water concentrates in the portions of the oxidation-promoting agent particles or the catalyst particles, whereby the resin composition is swollen, and the outer surface of the container becomes rugged.

In the oxygen-absorbing agent particles preferably used in the present invention, on the other hand, the layer of the oxidation-promoting agent or the catalyst stably remain being firmly adhered to the surfaces of the reducing iron particles even after melt-kneaded together with the thermoplastic resin. Therefore, the water absorbed by the oxidation-promoting agent or the catalyst readily activates the reducing iron powder, whereby absorption of oxygen is promoted by the oxidizing reaction of iron and the oxygen-absorbing rate is maintained at a high level. Moreover, the appearance is prevented from being deteriorated by the

occurrence of swelling and cracks, since the water absorbed by the oxidation-promoting agent or the catalyst is effectively utilized for the generation of hydrated oxides or the like.

In the present invention, it is important that the oxidation-promoting agent or the catalyst is present in an amount of from 0.1 to 5% by weight and, particularly, from 0.2 to 3.0% by weight per the reducing iron powder. When the amount of the oxidation-promoting agent or the catalyst is smaller than the above-mentioned range, the oxygen-absorbing rate becomes smaller than that of when the above-mentioned amount lies within the range of the present invention. When the above-mentioned amount is larger than the above-mentioned range, on the other hand, the resin composition as a whole loses resistance against the water and other properties, which is not desirable.

It is further important that the oxygen-absorbing agent particles used in the present invention have a specific surface area of not smaller than $0.5 \text{ m}^2/\text{g}$ and an apparent density of not larger than 2.2 g/cc in addition to the above-mentioned essential constitution. When the specific surface area is not larger than $0.5 \text{ m}^2/\text{g}$ or when the apparent density is not smaller than 2.2 g/cc , the oxygen-absorbing rate decreases as will be exemplified in Comparative Example 2 described later, and the amount of

residual oxygen in the container becomes considerably larger than that of when the specific surface areas and the apparent densities lie within the above-mentioned ranges. This is presumably due to that the resin composition blended with the oxygen-absorbing agent absorbs oxygen through the surfaces of the oxygen-absorbing agent particles, and oxygen is not effectively absorbed through the surfaces of the particles when the oxygen-absorbing agent particles have a specific surface area and an apparent density that lie outside the above-mentioned ranges.

It is desired that the oxygen-absorbing agent particles have a flat shape or a spindle shape having a compression degree (as measured by a method that will be described later) of not smaller than 20% and, particularly, from 30 to 90% and wherein not less than 50% of the particles have an average particle diameter of from 10 to 50 μm as measured by the laser-scattering method and an aspect ratio (short axis size/long axis size) of not larger than 0.6. The oxygen-absorbing agent particles having an average particle diameter within the above-mentioned range exhibits excellent dispersion in the thermoplastic resin and excellent oxygen-absorbing property. When use is made of the oxygen-absorbing agent particles having a compression degree of smaller than 20% or in which less

than 50% of the particles have an aspect ratio of not larger than 0.6, the exhibited oxygen-absorbing performance is inferior to that of the oxygen-absorbing agent particles lying within the preferred range of the present invention, and the container exhibits inferior appearance. This is considered to be that decreasing the aspect ratio or increasing the compression degree, i.e., increasing the degree of flatness, makes it possible to increase the surface areas of the particles and, hence, to increase the oxygen-absorbing rate, to orient the oxygen-absorbing agent particles in the direction of melt-flow of the resin composition, i.e., in the direction of the layers, contributing to preventing the swelling in the direction of the thickness and the occurrence of cracks.

The oxygen-absorbing agent particles used in the present invention are in no way limited thereto only. Desirably, the oxygen-absorbing agent particles are obtained by dry-milling a reducing iron powder and a powder of the oxidation-promoting agent or the catalyst. In the dry-milling, the powder of the oxidation-promoting agent or the catalyst is milled and is rubbed against the surfaces of the reducing iron particles so as to form a layer that becomes a firmly adhered coating layer. The formation of the firmly adhered coating layer is never accomplished by a conventional simple blending method or a method in which

the reducing iron powder is mixed with an aqueous solution of the oxidation-promoting agent or the catalyst and is dried. In addition, the dry-milling accomplishes the actions of desirably adjusting the particle sizes of the reducing iron powder and controlling the flatness of the reducing iron powder particles to lie within the above-mentioned range.

In the present invention, the above-mentioned oxygen-absorbing agent particles are blended in an amount of from 5 to 200 parts by weight, particularly, from 10 to 100 parts by weight per 100 parts by weight of the thermoplastic resin. When the blended amount of the oxygen-absorbing agent particles is smaller than the above-mentioned range, the oxygen-absorbing property tends to considerably decrease than that of when the blended amount of the oxygen-absorbing agent particles lies within the range of the present invention. When the blended amount of the oxygen-absorbing agent particles is larger than the above-mentioned range, on the other hand, molding into the container and the physical properties of the container tend to be considerably deteriorated than those of when the blended amount of the oxygen-absorbing agent particles lies within the range of the present invention. These tendencies are not preferable.

In the present invention, it is particularly

preferable that the thermoplastic resin be a blended product of a plurality of substantially incompatible thermoplastic resins. The blended product of a plurality of substantially incompatible thermoplastic resins, when melt-molded, takes a multi layer-distributed structure in which each component is distributed in a layered form, and each layer overlaps on each other in the direction of the thickness and expands in the direction of the plane. Therefore, with the resin composition blended with the oxygen-absorbing agent obtained from this blended product, peeling is easily developed between the layers of each component, and even if the expansion of volume due to the oxidization of the reducing iron powder or swelling due to the water or the like is slightly caused, the swelling will be in a flat form in the direction of the plane, thereby the occurrence of ruggedness on the surface can be considerably reduced, as well as the occurrence of cracks in the direction of the thickness can be effectively prevented.

(Oxygen-absorbing agent particles)

The oxygen-absorbing agent particles used in the present invention comprise a core particle of a reducing iron powder, and a layer of oxidation-promoting agent or a catalyst firmly adhered and coated thereon.

The reducing iron powder is generally obtained by

reducing an iron oxide (e.g., mill scale) formed in the step of producing a steel with coke, milling the formed sponge iron, followed by finish-reduction in a hydrogen gas or a cracked ammonia gas, electrolytically precipitating iron from an aqueous solution of iron chloride obtained through the step of washing with acid, followed by milling and finish-reduction. That is, iron oxides such as iron rust formed on the surfaces of the product in the step of producing a steel are relatively in a pure form, and iron chloride obtained by washing the iron rust with acid is in a pure form, too. Iron oxide is reduced by firing at a temperature of, generally, from about 600 to about 1200°C.

The production of reducing iron is not limited to reducing iron washed with acid by firing, but includes spraying molten iron into a nonoxidizing atmosphere, milling pure metal iron, and thermally decomposing iron carbonyl with water vapor, provided the starting iron is in a pure form.

The reducing iron powder should have properties lying within ranges mentioned above. To prevent the resin from being deteriorated and to improve flavor-retaining property, however, it is desired that copper is contained in an amount of not larger than 150 ppm and sulfur is contained in an amount of not larger than 500 ppm with respect to iron.

As the oxidation-promoting agent or the catalyst for being firmly adhered and coated to the surfaces of the reducing iron powder, there can be exemplified a water-soluble or deliquescent inorganic electrolyte. Concrete examples include inorganic salts such as sodium chloride, calcium chloride, zinc chloride, ferrous chloride, ferric chloride, ammonium chloride, ammonium sulfate, sodium sulfate, magnesium sulfate, disodium hydrogenphosphate, sodium diphosphate, potassium carbonate and sodium nitrate.

Among them, it is particularly desired to use a chloride of an alkali metal or an alkaline earth metal and, particularly, sodium chloride, calcium chloride or ferric chloride. Use of a manganese salt such as manganese chloride (MnCl_2) or the like in addition thereto is effective in absorbing oxygen since the oxidation is promoted.

As the oxidation-promoting agent, there can be effectively used a water-soluble organic compound, such as glucose, fruit sugar, sucrose, gelatin, modified casein, modified starch, tragacanth gum, polyvinyl alcohol, CMC, sodium polyacrylate or sodium alginate. These organic oxidation-promoting agents or catalysts may be mixed into the thermoplastic resin in the form of oxygen-absorbing agent particles, or may be mixed into the resin separately from the oxygen-absorbing agent particles. In the present

invention, it needs not be pointed out that a plurality of oxidation-promoting agents or catalysts can be used in combination.

In the present invention, the reducing iron powder and the oxidation-promoting agent or the catalyst are used in combination at a ratio as described above in detail. The formation of the firmly adhered coating of the oxidation-promoting agent or the catalyst to the surfaces of the reducing iron powder is carried out by dry-milling the reducing iron powder and the powder of the oxidation-promoting agent or the catalyst. The end point of the dry-milling can be learned as the presence of the free solid particles of the oxidation-promoting agent or the catalyst become no longer confirmed through an electron microscope. As the dry-milling, there can be used such as vibration mill, ball mill, tube mill or super mixer. Though generally not required, the free fine powder of the oxidation-promoting agent or the catalyst can be removed, by sieving or by classification with wind power, from the oxygen-absorbing agent particles obtained after the dry-milling.

(Resin composition blended with oxygen-absorbing agent particles)

According to the present invention, the oxygen-absorbing agent particles are blended in an amount of from

5 to 200 parts by weight, particularly from 10 to 100 parts by weight per 100 parts by weight of the thermoplastic resin.

The thermoplastic resin includes polyolefins, for example, low-density polyethylene, linear low-density polyethylene (LLDPE), high-density polyethylene, polypropylene, poly-1-butene, poly-4-methyl-1-pentene and random or block copolymer of α -olefins such as ethylene, propylene, 1-butene, or 4-methyl-1-pentene; ethylene/vinyl compound copolymer such as ethylene/vinyl acetate copolymer, ethylene/vinyl alcohol copolymer, and ethylene/vinyl chloride copolymer; styrene resins such as polystyrene, acrylonitrile/styrene copolymer, ABS, and α -methylstyrene/styrene copolymer; polyvinyl compound such as polyvinyl chloride, polyvinylidene chloride, vinyl chloride/vinylidene chloride copolymer, polymethyl acrylate, and polymethyl methacrylate; polyamides such as nylon 6, nylon 6-6, nylon 6-10, nylon 11 and nylon 12; thermoplastic polyesters such as polyethylene terephthalate and polybutylene terephthalate; polycarbonate, polyphenylene oxide, or mixtures thereof.

The thermoplastic resin blended with the oxygen-absorbing agent has preferably the oxygen permeability, and from this standpoint, an olefin resin is particularly suitable. On the other hand, the olefin resin has a low

water-keeping property, and therefore, it causes the occurrence of swelling. By using a certain oxygen-absorbing agent, however, water supply which is necessary for the oxygen absorption can be smoothly performed.

In the present invention, it is particularly preferable from the standpoint of appearance that a blended product of a plurality of substantially incompatible thermoplastic resins or elastomers be used as the resin matrix blended with the oxygen-absorbing agent.

Examples of the thermoplastic elastomer include ethylene-propylene rubber (EPR), ethylene-propylene-diene rubber (EPDM), thermoplastic elastomer such as styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, styrene hydride-butadiene-styrene block copolymer, styrene hydride-isoprene-styrene block copolymer, hydrogenated butadiene-isoprene block copolymer, nitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), polybutadiene (BR), polyisoprene (IIB), butyl rubber, natural rubber, thermoplastic polyurethane, silicone rubber and acrylic rubber. Among them, a hydrocarbon elastomer and, particularly, EPR and EPDM are preferred.

In the present invention, though there is no particular limitation, examples of the combination of incompatible thermoplastic resins or elastomers include

propylene polymer/ethylene polymer, polyamide/olefin resin, polyamide/styrene resin, polyamide/ABS resin, polyethylene terephthalate/polybutylene terephthalate, polycarbonate/polystyrene resin, polyester resin/olefin resin, and polycarbonate/polyester resin.

A combination of resins particularly suited for the object of the present invention is that of a crystalline propylene polymer and an ethylene polymer, facilitating the dispersion of the oxygen-absorbing agent and heat-molding. As the crystalline propylene polymer, there can be used a homopolypropylene as well as a random or a block copolymer containing ethylene in an amount of from 1 to 20% by weight and, particularly, from 2 to 15% by weight. These polypropylenes may have an isotactic structure or a syndiotactic structure.

Examples of the ethylene polymer include high-density polyethylene (HDPE), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLPDE), at least one copolymer of ethylene and other olefin such as propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, or decene-1, and ethylene/vinyl acetate copolymer, ethylene/acrylate copolymer, ionomer, etc.

The ratio of one resin and other resin in the resin matrix can be varied over a wide range and, desirably, from

100:1 to 1:1 and, particularly, from 50:1 to 3:2 on the weight basis.

In the present invention, it is allowable to use a compatibility-imparting agent to adjust the degree of dispersion of the resins or elastomers in the resin complex matrix. The compatibility-imparting agent works to enhance the mutual action among different polymers, and is a block copolymer or a graft copolymer having the same components as the polymers A, B to be blended, is a block copolymer or a graft copolymer having a third component to be mixed in the form of molecules into either one of the polymer A or B to be blended, or is a graft copolymer of two polymers compatible with either one of the polymer A or B to be blended.

When attention is given to the functions, the compatibility-imparting agents are grouped into two, i.e., compatibility-imparting agents of the non-reaction type and compatibility-imparting agents of the reaction type. Examples of the former compatibility-imparting agent include styrene-ethylene-butadiene block copolymer, polyethylene-methyl polymethacrylate block copolymer and polyethylene-polystyrene block copolymer. Examples of the latter compatibility-imparting agent include maleic anhydride-modified olefin resin and, particularly, maleic anhydride-grafted polypropylene and polyethylene, styrene-

maleic anhydride copolymer, ethylene-glycidyl methacrylate copolymer, ethylene-acrylic ester-maleic anhydride copolymer, and styrene-glycidyl methacrylate copolymer.

These compatibility-imparting agents can be made present in the resin matrix in an amount of from 1 to 20% by weight and, particularly, from 2 to 10% by weight.

The oxygen-absorbing agent and the resin matrix may be mixed together by either the so-called dry-blending or melt-blending. In order to favorably disperse the oxygen-absorbing agent, furthermore, a resin composition (master batch) containing the oxygen-absorbing agent at a high concentration may be prepared and may then be mixed into the resin matrix.

(Packaging container)

The oxygen-absorbing packaging container may have any layer constitution so far as the thermoplastic resin layer containing an oxygen-absorbing agent is included in the container wall. In general, it is desirable from the viewpoint of the sanitary properties and the appearance that the thermoplastic resin layer without blended with the oxygen-absorbing agent is laminated on both sides of the resin composition blended with the oxygen-absorbing agent.

Referring to Fig. 2 illustrating a multi-layer

structure of a packaging container of the present invention, a container wall 1 comprises an outer layer 2 of a moisture-resistant thermoplastic resin, an adhesive resin layer 3a according to need, a first intermediate layer 4 of a gas-barrier resin, an adhesive resin layer 3b according to need, a second intermediate layer 5 of a resin composition blended with an oxygen-absorbing agent, and an inner layer 6 of a moisture-resistant thermoplastic resin. The second intermediate layer is a thermoplastic resin layer blended with an oxygen-absorbing agent, the thermoplastic resin comprising a plurality of substantially incompatible thermoplastic resins or elastomers. Attention should be given to that the second intermediate layer is formed on the inside of the gas-barrier resin layer 4.

Referring to Fig. 3 illustrating another multi-layer structure of a packaging container of the present invention, a container wall 1 comprises an outer layer 2 of a moisture-resistant thermoplastic resin, an adhesive resin layer 3a, a first intermediate layer 4 of a gas-barrier resin, an adhesive resin layer 3b, a second intermediate layer 5 of a resin composition blended with an oxygen-absorbing agent, a third intermediate layer 7 of a resin composition blended with an adsorptive deodorant, and an inner layer 6 of a moisture-resistant thermoplastic resin.

The oxygen-absorbing agent and the adsorptive deodorant are separately blended in the second intermediate layer 5 and in the third intermediate layer 7. It will be understood that the gas barrier resin layer 4, the oxygen-absorbing agent layer 5, and the adsorptive deodorant layer 7 are arranged in this order from the outer side.

The thermoplastic resin layer to be provided on both sides of the resin layer blended with the oxygen-absorbing agent will be a moisture-resistant resin (which absorbs little water) and, particularly, a thermoplastic resin having a coefficient of water absorption of not larger than 0.5% and, particularly, not larger than 0.3% as measured in compliance with ASTM D 570. Representative examples include olefin resins such as low-, medium- or high-density polyethylene, isotactic polypropylene, ethylene-propylene copolymer, polybutene-1, ethylene-butene-1 copolymer, propylene-butene-1 copolymer, ethylene-propylene-butene-1 copolymer, ethylene-vinyl acetate copolymer, ionically crosslinked olefin copolymer (ionomer) or a blend thereof, as well as styrene resins such as polystyrene, styrene-butadiene copolymer, styrene-isoprene copolymer and ABS resin, and thermoplastic polyesters such as polyethylene terephthalate, polytetramethylene terephthalate, etc or polycarbonates.

Among them, it is desired to use an olefin resin from the standpoint of sanitation and a propylene resin from the standpoint of heat resistance.

In the packaging container of the present invention, as a gas-barrier resin used as required there is used a heat-moldable thermoplastic resin having a low oxygen permeability. The most preferred example of the gas-barrier resin will be an ethylene-vinyl alcohol copolymer such as a saponified product of a copolymer obtained by saponifying an ethylene-vinyl acetate copolymer having an ethylene content of from 20 to 60 mol% and, particularly, from 25 to 50 mol% such that the degree of saponification becomes not smaller than 96 mol% and, particularly, not smaller than 99 mol%. It is desired that the saponified product of the ethylene-vinyl alcohol copolymer has a molecular weight large enough for forming a film and a viscosity of, generally, not smaller than 0.01 dl/g and, particularly, not smaller than 0.05 dl/g as measured in a mixture solvent of phenol and water at a weight ratio of 85:15 at a temperature of 30°C.

As another example of the gas-barrier resin having the above-mentioned properties, there can be used polyamides having amide groups in a number of from 5 to 50 and, particularly, from 6 to 20 per 100 carbon atoms,

such as nylon 6, nylon 6,6, nylon 6/6, 6 copolymer, metaxylylene adipamide, nylon 6, 10, nylon 11, nylon 12, and nylon 13. These polyamides, too, should have molecular weights large enough for forming films and a relative viscosity (η_{rel}) of not smaller than 1.1 and, particularly, not smaller than 1.5 as measured in concentrated sulfuric acid of a concentration of 1.0 g/dl at a temperature of 30°C.

The gas-barrier resin can be so provided as to neighbor the resin layer blended with the oxygen-absorbing agent as shown in Fig. 2.

In laminating the layers, a sufficient degree of adhesiveness will not be often obtained between the gas-barrier resin and the moisture-resistant thermoplastic resin as in the case of the ethylene/vinyl alcohol copolymer. In this case, an adhesive resin layer is interposed between them.

As the adhesive resin, there can be exemplified a thermoplastic resin having carbonyl ($-C-$) groups based on

$$\begin{array}{c} \parallel \\ O \end{array}$$

carboxylic acid, carboxylic anhydride, carboxylate, amide carboxylate or carboxylic ester in the main chain or in the side chain at a concentration of from 1 to 700 milliequivalent (meq)/100 g of the resin and, particularly, from 10 to 500 meq/100 g of the resin.

Suitable examples of the adhesive resin include ethylene-acrylic acid copolymer, ionically crosslinked olefin copolymer, maleic anhydride-grafted polyethylene, maleic anhydride-grafted polypropylene, acrylic acid-grafted polyolefin, ethylene-vinyl acetate copolymer, copolymerized polyester and copolymerized polyamide, which may be used in one kind or in a combination of two or more kinds. These resins can be effectively laminated by the simultaneous extrusion or by sandwich lamination. Furthermore, a thermosetting adhesive resin of the isocyanate type or the epoxy type can be used for adhering the gas-barrier resin film that has been formed and the moisture-resistant resin film.

It is desired that the resin layer blended with the oxygen-absorbing agent has a thickness of generally from 10 to 200 μm and, particularly, from 20 to 150 μm though it may vary depending upon the amount of oxygen permitted to be contained in the container and the shape of the container.

On the other hand, the moisture-resistant resin layer has a thickness of generally from 20 to 500 μm and, particularly, from 50 to 300 μm when it is provided on both sides of the resin layer blended with the oxygen-absorbing agent, and has a thickness which is from 0.2 to 30 times as

great and, particularly, from 0.5 to 10 times as great when it is provided as an intermediate layer. The inner layer and the outer layer may have an equal thickness, or either the inner layer or the outer layer may have a thickness larger than the other.

It is desired that the gas-barrier resin layer has a thickness of generally from 5 to 100 μm and, particularly, from 10 to 50 μm .

The packaging container of the present invention can be produced by a method that has been known per se.

For example, the container can be produced by the multi-layer simultaneous extrusion, and the resin or the resin composition is melt-kneaded by the extruders corresponding to each resin layer, and is extruded into a predetermined shape through a multi-layer multiple die such as T-die or circular die. Furthermore, the resin or the resin compositions is melt-kneaded by the injection machine corresponding to each resin layer, co-injected or successively injected into an injection metal mold thereby to prepare a multi-layer container or a preform for the container. It is also allowable to employ a layer lamination system such as dry lamination, sandwich lamination or extrusion coating.

The molded article may assume the form of a film, a sheet, a parison or a pipe for forming bottle or tube, or a

preform for forming bottle or tube. The bottle is easily formed from the parison, pipe or preform by pinching off the extruded product in a pair of split molds and blowing a fluid therein. Further, the pipe or preform is cooled and is, then, heated at a drawing temperature, drawn in the axial direction, and is blow-drawn in the circumferential direction utilizing the fluid pressure to obtain draw-blown bottles.

Furthermore, the film or the sheet is subjected to such means as vacuum molding, compressed-air molding, reverse draw forming or plug-assisted molding to obtain a packaging container in the form of a cup, tray, etc.

Furthermore, the multi-layer films can be overlapped or folded like a bag, followed by heat-sealing the periphery to obtain a bag-like container.

[Packaging body]

The packaging container of the present invention can be effectively used as a sealed packaging container for sterilizing the content with hot water, for hot-filling the content or for heating the content for retort sterilization etc. The multi-layer plastic container of the present invention can be further effectively used as a packaging container for cooking the content by heating it by microwaves in a microwave oven after the content sealed therein is taken out. As the content to be filled, the one

having the water content of not less than 50% is especially suitable, from the standpoint of the oxygen absorbing property.

In an ordinary state, the gas-barrier resin layer works to prevent the permeation of oxygen, i.e., to shut off oxygen. Under the conditions where the water and heat act simultaneously such as in the sterilization by heat, the oxygen-absorbing agent present in the intermediate resin layer effectively works to shut off oxygen. Thus, the functions are effectively shared depending upon the state where the container is placed. That is, under the conditions where the water and heat act simultaneously, the water permeates conspicuously through the moisture-resistant resin layer and the gas-barrier resin loses its original oxygen-barrier property due to the absorption of moisture, and further due to the rise in temperature. However, the water that is absorbed and the heat that is given activate the oxygen-absorbing agent which, then, effectively traps oxygen, thus eventually suppressing the permeation of oxygen during the sterilization by heat.

EXAMPLES

The invention will be further described by way of Examples. In the following Examples, measurements were taken in a manner as described below.

[Apparent Density]

Measured in compliance with JIS K 6721 maintaining a gap of 38 mm between the flow-out stopper of the funnel and the receiving unit. The receiving unit is of a cylindrical shape having a content of 5 cm³. A sample to be measured is poured into the funnel and is stopped immediately after the receiving unit is filled with the sample and the sample starts over-flowing. The powder swelling on the receiving unit is flatly scraped off along the upper end of the receiving unit using a spatula paying attention so as not to give vibration thereto. The powder adhered on the outer side of the receiving unit is mildly removed, and the powder is weighed by weighing the weight of the cup.
[Packed Apparent Density and Degree of Compression]

The receiving unit is filled with the powder up to its upper end like the case of measuring the apparent density. The receiving unit filled with the powder is horizontally raised by 3 cm and is allowed to fall. This operation is repeated 30 times, and the powder is further poured into space formed at the upper end of the receiving unit as the powder is compressed. The receiving unit is similarly allowed to fall another 30 times to compress the powder. The powder is poured into space formed in the receiving unit, and the receiving unit is allowed to fall another 6 times. Finally, the upper end is flatly scraped off, and the receiving unit is accurately weighed to find a packed

apparent density.

The compression degree is calculated in compliance with the following formula,

$$\frac{(\text{Packed apparent density}) - (\text{apparent density})}{(\text{Packed apparent density})} \times 100 (\%)$$

[Specific Surface Area]

Measured in compliance with the BET one-point method. The measuring device is of the Shimazu Flow-sorb type.

[Particle Diameter]

Measured in compliance with the laser diffraction-scattering method. The measuring device is a particle diameter distribution measuring device of the Shimazu laser diffraction type, SALD1100, and ethanol is used as a dispersion medium for the particles. Fifty-percent particle diameter is regarded to be an average particle diameter.

[Aspect Ratio]

The oxygen-absorbing agent particles are expanded into 250 times, photographed, and the aspect ratio is found from the formula $R = b/a$ wherein a denotes the length of the longest axis of the particle and b denotes the length of an axis that intersects the middle point of the long axis at

right angles.

(Example 1)

100 Parts by weight of a reducing iron powder produced from an iron ore and granulated to 2.4 mm to 12 mm and 2 parts of sodium chloride (NaCl) having an average particle diameter of 20 μm were introduced in a total amount of 1.5 kg into a vibration mill of a capacity of 3.0 liters together with steel balls, and were vibration-milled for 3 hours thereby to rub NaCl onto the surfaces of the iron powder. After the operation was finished, the NaCl powder could no longer be confirmed by eyes. The thus prepared NaCl-adhered iron powder (hereinafter referred to as adhered adsorbing agent) possessed a specific surface area of 1.8 m^2/g , an apparent density of 1.7 g/cm^3 and an average particle diameter of 28 μm . A polypropylene (PP) having an MI of 0.6 (g/10 min, 230°C) blended with 30% by weight of the adhered adsorbing agent was pelletized.

A 2-kind 3-layer sheet (having a total thickness of 210 μm , constitution ratio of white PP:PP:white PP = 1:1:1) was prepared having an intermediate layer of a polypropylene (PO) blended with the adhered adsorbing agent and inner and outer layers of a white PP obtained by blending a PP having an MI of 0.6 with 8% by weight of titanium white, by using a molding apparatus comprising an inner layer extruder, an outer layer extruder, an

intermediate layer extruder, a feed block, a T-die, a cooling roll and a sheet take-up device. (Example 1)

100 Parts by weight of a reducing iron powder that has been milled to possess a specific surface area of $2.4 \text{ m}^2/\text{g}$ and an apparent density of 1.9 g/cm^3 and 2 parts of NaCl were introduced into a V-type mixer and were blended together for 30 minutes to prepare an absorbing agent. The PP blended with this absorbing agent was pelletized to prepare a 2-kind 3-layer sheet in the same manner as described above (Product of Comparative Example 1).

Test pieces (30 x 30 mm) prepared from these sheets were introduced into a gas-impermeable cup (having a volume of 85 ml) together with 1 ml of distilled water, and were heat-sealed with a heat-sealing closure member made of a gas-impermeable aluminum foil-laminated film, and were preserved at 50°C . After preserved for a predetermined period of time, the oxygen concentration in the container was measured, the oxygen-absorbing amounts of the sheets were found, and the appearance of the sheet pieces was observed. As shown in Table 1, the sheets exhibited increased oxygen-absorbing rates without any change in the appearance.

Table 1

	<u>Amount of absorbing oxygen (cc/cm²)</u>			<u>Appearance</u>
	<u>1 day</u>	<u>3 days</u>	<u>7 days</u>	
Example 1	0.08	0.14	0.15	no change
Comparative Example 1	0.01	0.03	0.04	rugged

(Example 2)

A 4-kind 6-layer sheet (having a total thickness of 0.8 mm, a constitution ratio of PP/ADH/EVOH/ADH/PO/PP = 40/1/10/1/20/10) was formed having a first intermediate layer of polypropylene pellets (PO) blended with an adhered absorbing agent having a specific surface area of 1.8 m²/g and an apparent density of 1.7 g/cm³, a second intermediate layer of an ethylene-vinyl alcohol copolymer (EVOH: ethyl content of 32 mol%, saponification degree of 99.6 mol%), an inner layer and an outer layer of a white PP obtained by mixing a titanium white pigment into a PP having a melt index (MI) of 0.5 g/10 min (230°C), and adhesive layers of a maleic anhydride-modified PP (ADH) having an MI of 1.0 g/10 min (230°C). The obtained sheet was heated at 190°C and was formed into a square cup having a depth of 30 mm and a volume of 115 ml in a manner that the PO layer was on

the inside of the EVOH layer by using a vacuum molding machine. The cup was filled with 1 ml of water and was heat-sealed with a gas-impermeable aluminum foil-laminated closure member in a nitrogen atmosphere. After retort sterilization at 120°C for 30 minutes, the cup was preserved in an atmosphere maintained at 30°C and 80%RH, and the oxygen concentration in the container was measured after every passage of a predetermined period of time.

(Product of Example 2)

As a comparative product, 100 parts of reducing iron that is suitably granulated and 2 parts of NaCl having an average particle diameter of 20 μm were introduced into the same vibration mill as that of Example 1 to prepare an adhered oxygen-absorbing agent having a final shape of a specific surface area of 0.4 m^2/g and an apparent density of 2.45 g/cm^3 . The same cup was formed by using the same molding machine as used in this Example, preserved in the same manner, and the oxygen concentration in the container was measured after every passage of a predetermined period of time (Comparative Example 2-1).

The results were as shown in Table 2. Furthermore, the same cup was formed by using the same sheet but using PP instead of PO, and the preservation testing was conducted (Comparative Example 2-2).

Table 2

Results (oxygen-barrier property of the container)

	<u>Oxygen concentration (%) in the container</u>					
	<u>Immediately after retorting</u>	<u>1W</u>	<u>2W</u>	<u>1M</u>	<u>2M</u>	<u>3M</u>
Example 2	0.08	0.11	0.16	0.16	0.30	0.42
Comparative Example 2-1	0.08	0.16	0.39	0.40	0.71	0.95
Comparative Example 2-2	0.29	0.84	1.45	1.94	3.02	3.58

(Example 3)

In the product of Example 1 of the invention, not less than 60% of the particles have an aspect ratio of from 0.25 to 0.60. Furthermore, the adhered absorbing agent has an apparent density of 1.7 g/cm³ but a packed apparent density (packed bulk density) of 2.8 and a compression degree of $(1 - 1.7/2.8) \times 100 = 39\%$. By using this adhered absorbing agent, a 4-kind 6-layer sheet of Example 2 was prepared.

(Product of Example 3)

To the reducing iron powder milled into a particle diameter of 40 μm was sprayed an NaCl aqueous solution such

that the ratio of iron and NaCl was 100:2. Then, the water was removed to obtain an adhered absorbing agent. The adsorbed absorbing agent exhibited a large apparent aspect ratio, and in which larger than 60% of the particles exhibited an apparent aspect ratio of not smaller than 0.6. By using this adhered absorbing agent, a 4-kind 6-layer sheet of Example 2 was formed (Comparative Example 3-1).

Cups of the same shape as that of Example 2 formed by using these sheets were filled with 1 ml of distilled water and were sealed in a nitrogen atmosphere. The retort sterilization was effected at 120°C for 30 minutes to observe the oxygen concentration in the containers and the interior of the containers. This product of the invention exhibited excellent effect for suppressing the oxygen concentration in the container compared with that of the comparative product, and further exhibited excellent appearance.

As a Comparative Example 3-2, furthermore, a cup of the same constitution was prepared by using, as a starting material, an oxygen-absorbing agent which has an apparent aspect ratio comparable to that of this product of the invention but to which was adhered no NaCl that is a reaction promoting agent. A cup (Comparative Example 3-3) prepared by using, as a starting material, an absorbing agent obtained by blending an iron powder having an aspect

ratio comparable to that of the Comparative Example 3-1, was similarly sterilization-treated, and the oxygen concentration inside therein and the appearance were inspected. The results were as shown in Table 3.

Table 3

	<u>Oxygen concentration (%) in the container</u>					<u>Appearance evaluation (5 steps)</u>
	<u>Immedi- ately after</u>	<u>1W</u>	<u>2W</u>	<u>1M</u>	<u>3M</u>	
Example 3	0.08	0.11	0.16	0.16	0.42	5 (good)
Comp.Ex.3-1	0.08	0.15	0.24	0.34	0.76	3
Comp.Ex.3-2	0.08	0.14	0.23	0.40	0.95	1
Comp.Ex.3-3	0.08	0.16	0.39	0.40	1.20	1 (poor)

(Example 4)

A sheet of Example 1 was prepared by using an oxygen-absorbing agent obtained by introducing an iron powder and sodium chloride (NaCl) into a vibration mill in the same manner as in Example 1, and an iron powder granulated in the same shape as the oxygen-absorbing agent of Example 1 and to which has been sprayed an aqueous solution

containing 20% of NaCl at a rate of 10 ml per 100 g of iron, followed by drying. After preserved for one day under the conditions of 50°C and 100%RH, the amount of absorbing oxygen of the sheet was measured. Both exhibited good oxygen-absorbing performance owing to the presence of the reaction promoting agent adhered to the surfaces of the iron powder, but the one obtained by the dry type method as in Example 1 exhibited an oxygen-absorbing amount of 0.11 cc/cm² and the one obtained by the wet type method using the aqueous solution of the reaction promoting agent exhibited an oxygen-absorbing amount of 0.07 cc/cm².

(Example 5)

A polypropylene having an MI of 0.6 (g/10 min, 23°C) was blended with 30% by weight of the oxygen-absorbing agent coated with the oxidation promoting agent prepared in Example 1, and was pelletized. Similarly, furthermore, a blend of a polypropylene having an MI of 0.6 and a low-density polyethylene (LDPE) having an MI of 0.5 at a ratio of 9:1, was pelletized. By using these pellets, 3-layer sheets of Example 1 were prepared (Trial Piece 5-1, 5-2) and were heat-sterilized at 120°C for 30 minutes.

Furthermore, a 3-layer sheet (Comparative Example 5-1) same as that of Example 1 prepared by using pellets of a mixture of PP having an MI of 0.6 and an oxygen-absorbing agent blended with the oxidation promoting agent used in

the comparative product 1 of Example 1, and a 3-layer sheet (Comparative Example 5-2) prepared by using pellets of a mixture of PP having an MI of 0.6 and an LDPE having an MI of 0.5, were heat-sterilized at 120°C for 30 minutes to examine a change in the appearance.

Properties were evaluated relying upon the method of measuring the amount of absorbing oxygen used in Example 1. The results were as shown in Table 4. As will be obvious from the results, use of a resin system of a mixture of PP with LDPE makes it possible to enhance the appearance as well as the oxygen-absorbing performance.

Table 4

	<u>Evaluation of appearance (5 steps)</u>	<u>Oxygen-absorbing ability (cc/cm²)</u>
Test Piece 5-1	4	0.09
Test Piece 5-2	5	0.11
Comparative Example 5-1	1	0.01
Comparative Example 5-2	3	0.02

Excellent 5 ↔ Poor 1

(Example 6)

A 4-kind 6-layer cup of Example 2 was prepared by using an oxygen-absorbing resin composition which was the product of the invention of Example 1. This cup was filled with 50 ml of distilled water, sealed under atmospheric pressure, heat-sterilized at 120°C for 30 minutes, and was then preserved at 30°C and 80%RH.

(Product of Example 6)

The test was also conducted by using a similar cup (Comparative Example 6) prepared by using pellets of iron and NaCl-blended oxygen-absorbing agent used in Comparative Example 1 in Example 1.

The product 6 of the invention exhibited no change in the appearance of the container over extended periods of time, but the Comparative Example 6 developed tiny cracks in the inner surface of the container.

(Effect of the Invention)

According to the present invention, the thermoplastic resin is blended with an oxygen-absorbing agent particles which comprise a reducing iron powder and a layer of an oxidation promoting agent or a catalyst firmly adhered and coated to the surfaces of the reducing iron powder, and having a predetermined specific surface area and an apparent density. It is thus made possible to provide a resin composition containing an oxygen-absorbing agent

featuring an enhanced oxygen-absorbing rate, without developing ruggedness after preserved for extended periods of time or after heat-sterilization, and exhibiting excellent appearance, as well as to provide packaging containers.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram schematically illustrating the structure of oxygen-absorbing agent particles that are favorably used in the present invention.

Fig. 2 is a sectional view illustrating a multi-layer structure of a container of the present invention; and

Fig. 3 is a sectional view illustrating another multi-layer structure of a container of the present invention.

DESCRIPTION OF REFERENCE NUMERALS

- 1: Container wall
- 2: Outer layer of the moisture-resistant thermoplastic resin
- 3a, 3b: Adhesive resin layer
- 4: First intermediate layer comprising a gas-barrier resin
- 5: Second intermediate layer comprising a resin composition blended with an oxygen-absorbing agent
- 6: Inner layer of the moisture-resistant thermoplastic resin

- 7: Third intermediate layer comprising a resin composition blended with an absorptive deodorant
- 10: Oxygen-absorbing agent particles
- 20: Reducing iron powder core particle
- 30: Layer of oxidation-promoting agent or catalyst

NAME OF THE DOCUMENT: ABSTRACT OF THE DISCLOSURE

ABSTRACT:

OBJECT: To provide a resin composition containing an oxygen-absorbing agent having an improved oxygen-absorbing rate, without developing ruggedness after preserved for extended periods of time or after heat-sterilization, and exhibiting excellent appearance, and to provide packaging containers formed from said resin composition.

MEANS: An oxygen-absorbing resin composition obtained by blending 10 to 200 parts by weight of oxygen-absorbing agent particles per 100 parts by weight of the thermoplastic resin, which comprises a reducing iron powder and an oxidation-promoting agent or a catalyst layer firmly adhered and coated to surfaces of said reducing iron powder, and which has a specific surface area of not smaller than $0.5 \text{ m}^2/\text{g}$ and an apparent density of not larger than 2.2 g/cc , and in which the oxidation-promoting agent or the catalyst is present in an amount of from 0.1 to 5% by weight per the reducing iron powder.

SELECTED DRAWING: None

Name of Document: Authoritatively amended data

Document amended: Application

Recognized information•Additional information

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